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A THERMOCHEMICAL GAS ANALYZER FOR CONTINUOUS DETECTION OF OXYGEN

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The thermochemical method of detecting the concentration of oxygen in gases is, as is well known, based on measuring the thermal effect (temperature) of the catalytic oxidation which occurs on an active catalyst bathed in the gas to be analyzed. In doing this, measuring the temperature of the catalyst is done either with a thermocouple inserted in a layer of the catalyst [1] or by two resistance thermometers connected in a bridge circuit [2]. One of the thermometers is placed in a chamber filled with the catalyst and the other — a compensating one — in a chamber with an inactive mass. The indicating instrument is graded in percentages of oxygen.

One of the newest and most perfect automatic instruments of the indicated type is the TKhG-5 gas analyzer [2, 3]. A catalyst working with a pre-heat of 120-130° is used in this instrument. The gas analyzer has a scale from 0 to 1.0% O_2 and is intended to detect oxygen in electrolytic hydrogen. The instrument uses 220 v a-c from a voltage regulator. The flow rate of the gas to be analyzed is 1 l/min at a pressure of 0.4-1 atm on entering the instrument. The

instrument's time constant is 2 minutes with an error of ± 10% of the maximum scale reading.

In research on flameless burning of hydrogen on a platinum and iridium platinum thermocouple done by the authors of the present article [4], they concluded that it would be possible to use a burner of simple construction for continuous detection of oxygen in gaseous mixtures. The principle of the burner's action consists in the following: by virtue of a catalytically active thermocouple placed over the opening of a tube whence a stream of hydrogen issues into a stream of gas containing oxygen, spontaneous flameless ignition of the hydrogen is excited and in this process the electromotive force originating because of the heat of the reaction is changed proportionally to the concentration of oxygen. But at an ordinary temperature the steady flameless burning of hydrogen occurs when there is 8-10% oxygen in the gas, but at lower concentrations because of the decrease in the quantity of heat developed during combustion it becomes unsteady and ceases.

The present work is devoted to studying the possibility of using flameless combustion of hydrogen on a catalytic thermocouple for the continuous measurement of concentrations of oxygen less than 10% by carrying out the process at an increased temperature.

Experimental Section

The special burner shown schematically in Fig. 1 was constructed for setting up the pertinent experiments.

On metallic base 1 is fixed porcelain column 2 bearing ceramic drum 3. In grooves in the drum is placed the heating coil 4 and its ends led out through insulator 9. Through the central aperture in the column porcelain tube 5 is passed to deliver hydrogen; on the upper

end of the tube are affixed insulators 6. On them are fastened the wires of the platinum and iridium platinum thermocouple whose working junction 7 is placed 2-3 mm above the aperture of central tube 5 supplying hydrogen. Tube 5 of diameter of 2 mm has a bore of 0.5 mm. The "cold" junctions of the catalytic thermocouple are led out for 0.5 mm from tube 5 and 1 mm below its end. The arrangement of the cold junctions at a sufficiently short distance from the working junction ensures isothermal conditions for all three junctions of the catalytic thermocouple when there is no flameless combustion. In addition to that, when hydrogen is being supplied and is burning flamelessly on the working junction a similar process cannot occur on the cold junctions, since diffusion of the hydrogen toward them, i.e., counter to the flow of gas, is inhibited.

Leads 10 from the cold junctions are led through insulators 11 and 12. On a level with the junctions of the catalytic thermocouple is aligned the junction of chromel-aluminum thermocouple 13 for measuring the temperature of the gas.

The gas to be analyzed is led into the burner through tube 15 passed through the base and goes out of the burner through the upper opening in glass envelope 16. The envelope about 50 ml in volume is joined to the base with the sealing nut 17 on a rubber gasket and is provided with asbestos heat insulation covered on the outside by a sheet metal box. The platinum and iridium platinum thermocouple (10% iridium platinum) of 0.18 mm diameter wires was activated by an earlier described method [4] under conditions of flameless hydrogen combustion on it.

The above described catalytic thermocouple setup afforded good leveling of the temperature of its junctions and guaranteed an emf

of practically zero in the absence of combustion. When the temperature of the gas changed in the 20-400° range the emf did not exceed 0.05 mv, and in the 150-300°C range equalled zero. Testing was by measuring the emf with a millivoltmeter (class 0.5) while passing air through the burner with a velocity of 300 ml/min and varying the temperature of the gas within wide limits.

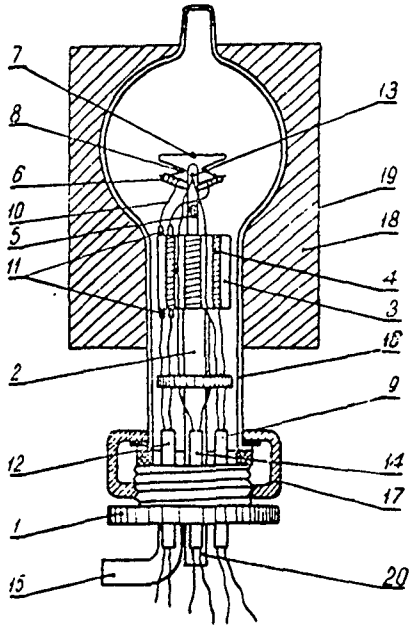

Fig. 1. Diagram of burner. 1) base; 2) porcelain column; 3) ceramic drum; 4) heating coil; 5) tube supplying hydrogen; 6) porcelain insulators; 7) working junction of the platinum and iridium platinum thermocouple; 8) "cold" junctions of the platinum and iridium platinum thermocouple; 9) insulator of leads from heating coil; 10) leads from cold junctions; 11 and 12) insulator of leads from catalytic thermocouple; 13) chromel-aluminum thermocouple; 14) insulator; 15) tube for delivering a mixture of nitrogen and oxygen; 16) glass envelope; 17) sealing nut; 18) heat insulation; 19) sheet metal box; 20) outlet of tube supplying hydrogen.

Flameless hydrogen combustion on the activated thermocouple occurred spontaneously at a gas temperature of about 150° and above, because of the oxygen in the air, simultaneous with starting delivery of the hydrogen. At unchanged flow rates of the gases and temperature in the burner the emf had a strictly defined value. Study of the influence of heating the gas on the process of flameless hydrogen combustion showed that with an increase in the temperature to 250-300°C steady flameless hydrogen combustion at slight oxygen concentrations

(tenths of one percent) in the gas was observable. The below described experiments were conducted at a gas temperature in the burner of 270°C.

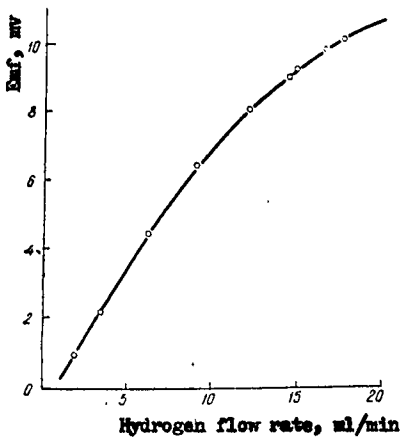

Fig. 2. Relationship of emf in platinum and iridium platinum thermocouple to hydrogen flow rate on delivering air (20.8% O_2) to the burner.

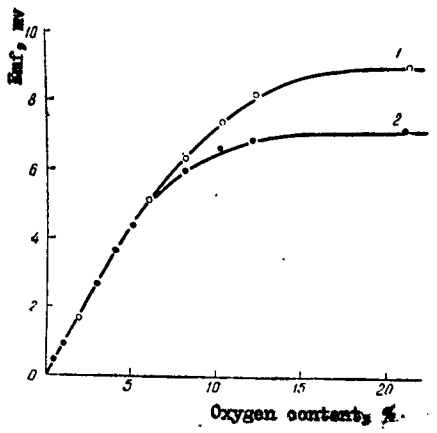

Fig. 3. Relationship of emf in platinum and iridium platinum thermocouple to oxygen content in nitrogen mixture. Gas temperature in the burner 270°, air flow rate 300 ml/min at 20°, at hydrogen flow rate of 1) 14.4 and 2) 11.0 ml/min.

The hydrogen, oxygen, and nitrogen were supplied from tanks and their flow rates were measured with rheometers. The streams of nitrogen and oxygen were directed into a mixer, from which they entered the burner. The oxygen concentration in the mixture was determined by volumetric gaseous analysis on a VTI apparatus. The samples were taken out with a three-branched pipe attached to the burner.

In order to determine the relationship of catalytic thermocouple emf to the oxygen content in the stream of gas it was necessary to secure a constant supply of hydrogen during the whole experiment. By using hydrogen from a tank at a pressure of 100-150 atm we were successful in regulating the flow rate of the hydrogen by the rheometer with

sufficient accuracy with a two-stage reducer. The required value of the hydrogen flow rate was selected empirically. Figure 2 shows the empirically found relationship of catalytic thermocouple emf to the hydrogen flow rate when air (20.8% O_2) is being supplied to the burner and the gas temperature therein is 270°C. Increasing the hydrogen flow rate to 17.2 ml/min caused the hydrogen to burst into flames in some cases; therefore the hydrogen flow rate was decreased to 14.4 ml/min in order to derive the relationship of the emf to the oxygen concentration. The results of the experiments are shown in Fig. 3 (curve 1). When oxygen-containing mixtures with a concentration of less than 1% O_2 were delivered to the burner, flameless combustion did not proceed completely steadily. For example, after purging the burner with nitrogen free from oxygen, when a mixture of 1% O_2 and 99% N was delivered, flameless hydrogen combustion on the thermocouple did not start up, which was ascertained by the absence of an emf, i.e., the instrument did not "feel" the slight concentrations of oxygen. This was explained by noting that the assigned hydrogen flow rate was too great and with a low oxygen concentration in the gas did not provide a sufficient influx of oxygen to the surface of the catalytic thermocouple, for this influx was being accomplished by diffusion of the oxygen through the stream of hydrogen bathing the working junction of the thermocouple. Therefore the flow rate of the hydrogen was lowered to 11 ml/min. In this case, when air was supplied to the burner the emf amounted to 7.3 mv. For the given hydrogen flow rate the relationship of the catalytic thermocouple emf to the oxygen content was derived (Fig. 3, curve 2). Steady flameless hydrogen combustion was observed at oxygen concentrations of 20.8 to tenths of a percent (by volume). The graph shows that at this hydrogen flow

rate the greatest sensitivity of the thermocouple to a change in the oxygen concentration was observed in oxygen content in the gas of up to 6%. A change in the emf of approximately 0.9 mv corresponded to a change in the oxygen concentration of 1%. At oxygen concentrations from 6 to 10% the change in the emf for each 1% O_2 amounted to about 0.3-0.4 mv.

When nitrogen-oxygen mixtures with higher oxygen content were passed through, the following became clear. With a hydrogen flow rate of 14.4 ml/min and an oxygen content of 20.8% in the gaseous mixture the catalytic thermocouple emf reaches 9.1 mv. Delivery of mixtures enriched to 40% O_2 caused bursting into flames, i.e., volumetric conversion of the reaction. But at a hydrogen flow rate of 11 ml/min an emf of 7.3 mv corresponded to a 20.8% O_2 concentration and raising the oxygen content in the mixture right up to 95% (by volume) did not cause the hydrogen to burst into flame. But when the oxygen concentration was raised above 21% no increase in the emf was observed at the prescribed hydrogen flow rate, which indicated an insufficient influx of hydrogen to the junction of the catalytic thermocouple. Thus, the hydrogen flow rate is an important factor, on which the sensitivity and accuracy of detection of the oxygen concentration by the emf of the catalytic thermocouple depends.

On studying the relationship of the value of the emf of the platinum and iridium platinum thermocouple to the temperature of the gas medium in the burner it was ascertained that in unchanged flow rates of hydrogen and oxygen-containing gas measured at 20°C and constant concentration of oxygen in the mixture, a certain decrease in the emf takes place with the rise in temperature. The reduction in the incandescence of the working junction of the catalytic thermocouple

may be observed visually.

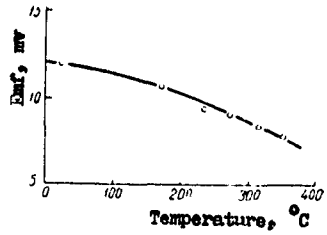

Fig. 4. Relationship of emf of platinum and iridium platinum thermocouple to temperature of gas in burner. Hydrogen flow rate 14.4 ml/min, air flow rate (20.8% O_2) 300 ml/min.

The observed effect of gas temperature on the intensity of flameless combustion and on the value of the emf of the catalytic thermocouple is possibly caused by the change in the velocities of flow of the hydrogen and oxygen-containing mixture, or is connected with partial volumetric conversion of the reaction.

A working device as a model of an automatic gas-analyzer for oxygen was built and tested on the basis of the experimental data.

The meter of the gas analyzer is schematically represented in Fig. 5. In order to curtail heat losses the meter is enclosed in a glass envelope made like a Dewar flask and hermetically sealed to its base. At a constant flow rate of gas containing oxygen entering via tube 10, and at a prescribed flow rate of hydrogen entering through tube 8 with the temperature of the gaseous medium in the element at 250-300°C there appears steady flameless hydrogen combustion on the working junction of the catalytically active platinum and iridium platinum thermocouple fixed 2-3 from the end of tube 8, and in this process the emf of the thermocouple is proportional to the oxygen concentration in the gaseous mixture. The cold junctions of the catalytic thermocouple are made of 0.15 mm wire located 2-3 mm below the end of the tube from which the hydrogen comes, so that when there is no combustion they have the same temperature as the working junction and the emf equals zero. Therefore the emf which appears in flameless hydrogen combustion as a result of increasing the junction temperature

because of the heat of chemical reaction under constant conditions depends only on the oxygen concentration.

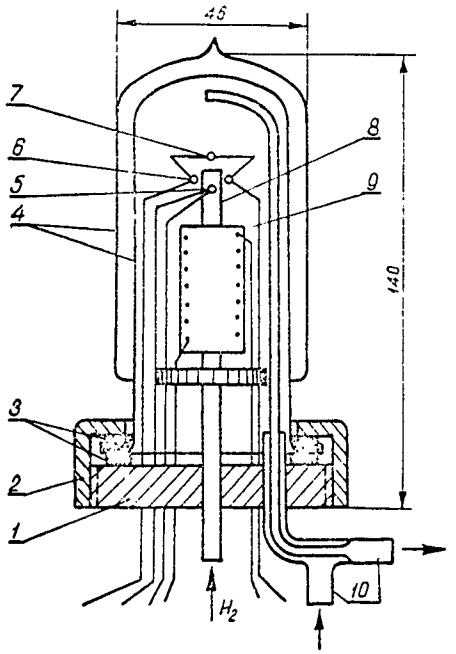

Fig. 5. Meter of the gas analyzer. 1) base; 2) sealing nut; 3) sealing gasket; 4) envelope with double walls with vacuum between them; 5) chromel-aluminum thermocouple; 6) cold junctions of platinum and iridium platinum thermocouple; 7) working junction of platinum and iridium platinum thermocouple; 8) tube for supplying hydrogen; 9) heating coil; 10) tubes for supplying and exhausting gas from the element.

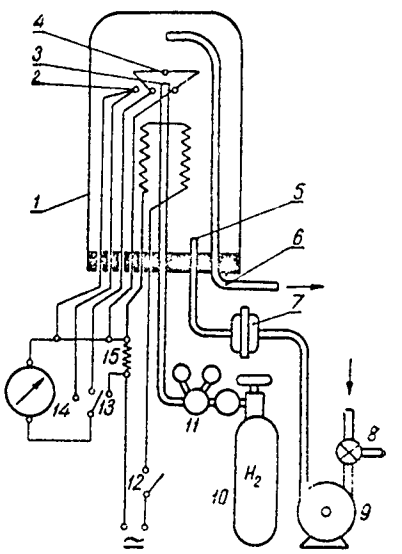

Fig. 6. Over-all diagram of setup for continuous detection of oxygen concentration in gas. 1) meter; 2) chromel-aluminum thermocouple; 3) tube for delivery of hydrogen; 4) junction of platinum and iridium platinum thermocouple; 5) tube for delivery of gas to be analyzed; 6) gas exhaust tube; 7) gas flow regulator; 8) valve for initiating delivery of air or gas to be analyzed; 9) gas blower; 10) hydrogen tank; 11) reducer; 12) heating coil switch; 13) three-pole switch; 14) indicating device (millivoltmeter); 15) constant resistance of manganin wire.

Figure 6 shows the laboratory setup for continuous detection of the oxygen content of a gas. The meter, the indicating device, and the electrical control system are assembled in a 300 x 180 x 60 mm wooden cabinet. Figure 7 shows its exterior view with controls. The

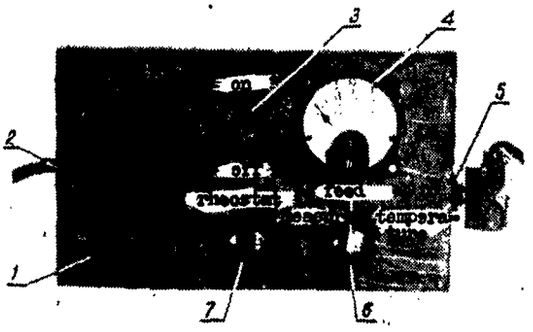

Fig. 7. View of cabinet of meter and controls. 1) body of case; 2) gas delivery; 3) switch handle; 4) indicating device (millivoltmeter of 12 mv); 5) heating coil contacts; 6) knob for switching the millivoltmeter to measure the voltage on the heating coil, temperature of gas in the element, and oxygen concentration; 7) knob of heating coil rheostat.

feed of the heating coil of the element is d-c with a voltage of about 30. The heating current was checked in its voltage drop across resistance 15 (Fig. 6) with indicator 14 (a millivoltmeter of 12 mv) with its dial marked in volts. Alternating current is also suitable for supplying the device; in that case a transformer and ammeter setup is necessary in addition. The gas to be analyzed was delivered with a small air current through a diaphragm flow regulator. Hydrogen was delivered from a small tank of 1 l capacity; its flow rate was regulated by a two-step reducer.

When the device is activated air is first delivered (air blower turner on) and the heating coil is turned on with handle 3 (Fig. 7) while the rheostat has been turned off by knob 7. Switch 6 is put on "temperature" and the indicating device is connected with the chromel-aluminum thermocouple and its needle moves to the right as the temperature of the gas in the meter rises. When the needle gets to the check mark "T" the working temperature of 270° has been reached. After this, switch 6 is put on "feed" and the voltage drop across the coil is checked with the indicating device. By turning knob 7 of the rheostat the needle becomes fixed at the known working mark on the voltage scale. After regulating thermocouple incandescence, switch 6 is put on "measure" and the needle of the indicator returns to the zero mark on the scale.

Hydrogen is then delivered to the device by turning the handle of the reducer on the hydrogen tank. In doing this flameless hydrogen combustion is initiated on the catalytic thermocouple and the needle of the indicator begins to move to the right. By regulating the supply of hydrogen the need is fixed at the check mark "HS". The hydrogen flow rate in this process corresponds to that prescribed at the scale marking. After regulating the hydrogen flow rate a turn of the valve on the gas lead switches from air to the gas to be analyzed and the indicator needle shows the percentage of oxygen in the gas. When the device is functioning, periodic checks of the gas temperature in the meter and regulation of the coil-heat are required, as was demonstrated above. The flow rate of the hydrogen is also periodically checked and regulated by delivering air to the device instead of the gas to be analyzed, and in doing this the indicator needle must stop on the check mark HS.

Mixtures of nitrogen and oxygen with a content of less than 10% O_2 were obtained by dispensing nitrogen from the compression tank with a rheometer into the air stream delivered by the blower. Along with recording the readings of the indicator, gas samples are bled off through the three-branched pipe for analysis on the VTI apparatus.

We may see from the graphs in Fig. 8 that steady flameless hydrogen combustion at a concentration of 1.8% O_2 began when hydrogen was delivered with a velocity of 1.5 ml/min (point B on curve 1). An increase in the hydrogen supply at first caused an increase in the emf of the catalytic thermocouple to a certain maximum value, and then a decrease. The maximum value of the emf attained by changing the hydrogen flow rate at various concentrations of oxygen was the larger, the higher the concentration of oxygen in the gas entering the meter. With an oxygen content of 1.8%, increasing the hydrogen flow rate above 15 ml/min led to cessation of flameless combustion on the thermocouple

(break in the curve at point C). This indicated that when the hydrogen flow rate is increased the access of oxygen to the surface of the catalytic thermocouple is inhibited.

The optimum hydrogen flow rate is defined by the graphs of the relationship of catalytic thermocouple emf to hydrogen flow rate at various oxygen concentrations in the gas; and perhaps the millivoltmeter scale is graduated according to the oxygen under the given conditions. Thus, from a comparison of the curves in Fig. 8 it is evident that it is possible to measure oxygen concentration up to 10% by assigning a hydrogen flow rate of not less than 2-3 ml/min and not more than 15 ml/min. The nature of the dependence of thermocouple emf on oxygen content in the mixture becomes clear when graphs are constructed for this dependence for several prescribed hydrogen flow rates, as is shown in Fig. 9. The pertinent emf values are taken from the graphs in Fig. 8. One of the derived curves corresponding to a definite hydrogen flow rate may be used as a calibration curve for constructing the scale of the millivoltmeter indicator.

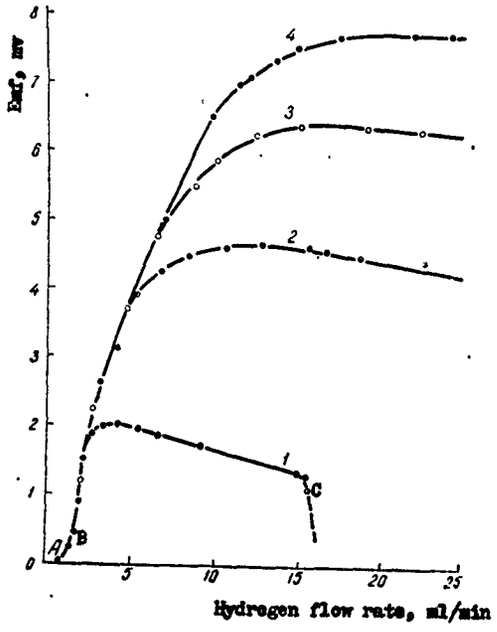

Fig. 8. Relationship of emf of platinum and iridium platinum thermocouple to hydrogen flow rate. (Gas temperature in the meter, 270°C; gas flow rate, 300 ml/min at 19°). Oxygen content in mixture: 1) 1.8%; 2) 5.0%; 3) 7.3%; 4) 10.0%.

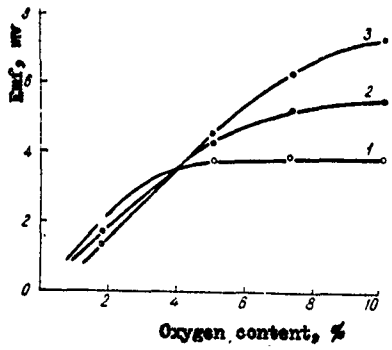

Fig. 9. Relationship of catalytic thermocouple emf to oxygen concentration in gas. Hydrogen flow rate ml/min: 1) 5; 2) 10; 3) 15.

The magnitude of the flow rate of the gas to be analyzed may be set within rather broad limits, beginning with 30-50 ml/min. To secure a sufficiently rapid gas exchange in the element, which is reflected in the time the device takes to react when measuring the oxygen concentration in the gas stream, it is expedient to have a somewhat larger flow rate of gas analyzed, on the order of 200-500 ml/min. Table 1 shows the effect of the magnitude of the flow rate of the gas to be analyzed on the emf of the catalytic thermocouple. With 2% O_2 in the gas an increase in the flow rate caused a certain increase in the emf, which should be explained by the presence of excess hydrogen in relation to the quantity of oxygen reaching the surface of the working junction of the thermocouple, whereas a decrease in the emf observed when the flow rate is increased and contains 20.8% O_2 is caused by limited combustion because of the diffusion of the hydrogen, the amount of which under these conditions obviously limits the combustion rate and the heating of the catalytic thermocouple.

It was also ascertained that in great changes in gas flow rate its temperature in the meter also changes somewhat, notwithstanding the steadiness of the heating current. But, as the data in Table 2 show, this effect is insignificant.

The satisfactory stability of the gas stream rendering the above indicated flow-rate fluctuation effect impalpable, is secured by the

diaphragm flow regulator developed in our laboratory. The principle of action of this regulator is similar to the one described in the literature [5].

TABLE 1

Relationship of emf of Platinum and Iridium Platinum Thermocouple to Flow Rate of Gas to be Analyzed. (Temperature of Gas in the Element, 257°; Hydrogen Flow Rate, 14.4 ml/min.)

Flow rate of analyzed gas at 20°C, ml/min.	EMF of catalytic thermocouple, mv.
On delivering a gaseous mixture containing 2.0% O_2	
200	1.15
220	1.30
250	1.45
280	1.65
300	1.73
400	1.75
On delivering air 20.8% O_2	
165	9.70
240	9.50
300	9.30
350	9.15

TABLE 2

Relationship of Gas (air) in Element to its Flow Rate When Heating Current is Constant (0.85 amp, 23 v) and to the Absence of Hydrogen and Flameless Combustion.

Gas flow rate, ml/min	90	180	300
Gas temperature in meter, °C	270	257	250

TABLE 3

Relationship of Gas Temperature in Burner to Voltage of Heating Current. (Gas Flow Rate, 300 ml/min.)

Voltage, v	0	13	20	22	23	25	26.8	29.5
Gas temperature, °C	20	170	237	257	270	292	311	350

When determining the oxygen concentration in an oxygen-nitrogen mixture when the oxygen content was changed within the limits from 1 to 10% and back by admixture of oxygen in the nitrogen stream, the error in the instrument's readings, determined by parallel analysis of samples on a VTI apparatus with $\pm$ 0.1% accuracy, amounted to

± 0.3-0.5%. On the instrument's scale marked off from 0 to 10% O_2 this corresponds to 5% of the maximum scale reading.

The limiting concentration which enables us to observe a displacement of the instrument's needle by 1 mm [sic] was approximately 0.2%. The calibrated hydrogen flow rate was 8 ml/min, the analyzed gas flow rate was 300 ml/min. It took 5-10 min. to get the device operational. The device reacted to a change in the oxygen content of the analyzed gas after approximately 20 seconds, counting from the moment of switching on the appropriate dispensing valve.

Among the merits of the described method of detecting oxygen must be reckoned the relative simplicity of the unit and the feasibility of creating an instrument for automatically measuring the concentration of oxygen over a rather wide range of concentrations with sufficient accuracy of measurement and rapidity of reaction.

The demonstrated feasibility of constructing a meter capable of functioning in a gaseous medium at temperatures above 200° also is of practical interest.

When evaluating the possibilities of the described method we should emphasize that a change in emf corresponding to 1% O_2 in mixture is sufficiently large (0.4-0.9 mv) and the emf can be measured with great accuracy. However the sensitivity and accuracy of measurement of small concentrations of oxygen by the given method is determined by the structural features of the meter and careful "tuning" of it, and also by the accuracy in dispensing the hydrogen and its steady flow rate. There is reason to assume that the indicated method may permit the obtaining of sensitivity and accuracy higher than those we observed in the described model.

The method is applicable for detecting oxygen in mixtures with incombustible gases and vapors, but perhaps modified; and applicable

to the detection of oxygen in some inflammable gases without using hydrogen.

Conclusions

1. A working model of a thermochemical gas analyzer for continuous detection of oxygen in gaseous mixtures containing up to 10% O_2 has been constructed and tested under laboratory conditions. The action of the gas analyzer is based on using the relationship of the emf of a platinum and iridium platinum thermocouple, on which flameless hydrogen combustion occurs at a temperature in the gaseous medium of 250-300° because of the oxygen in the gas to be analyzed to the oxygen concentration.

2. The research data may be used for developing an automatic gas analyzer for continuous detection of oxygen directly in a stream of hot gas.

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